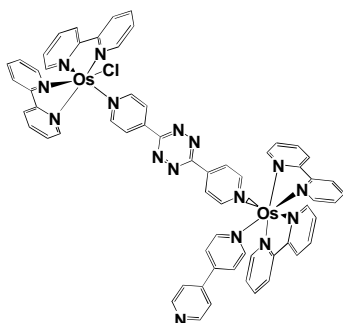


## ELECTROCHEMICAL VS. PHOTOINDUCED ELECTRON TRANSFER

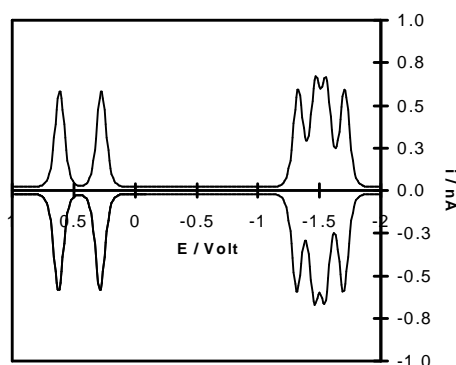
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The strength of electronic coupling, the distance of charge transfer and the nature of the bridge linking the reactants are of central importance in the dynamics of nearly all molecule based electron transfer reactions.<sup>1,2,3</sup> The development of spontaneously adsorbed and self-assembled monolayers have greatly facilitated investigations into these effects for heterogeneous electron transfer.<sup>4</sup> However, important issues such as the dynamics of electron cross-exchange, or comparisons of thermal vs. photochemically driven reactions, cannot be explored using traditional monolayers that contain a single redox center. In contrast, surface active dimers would allow these issues to be explored. Bridges that incorporate metal centers are expected to exhibit a different behavior compared to conventional organic linkers because their accessible redox states can act as switchable “sinks” thus modulating the dynamics of electron transfer.<sup>5</sup> Information about processes of this kind is especially important for molecular electronics applications ranging from information storage to the production of antennae complexes suitable for solar energy conversion.

In this contribution, we report on monolayers assembled on platinum microelectrodes using the dimeric complex  $[\text{pOp Os}(\text{bpy})_2 \text{ 4-tet Os}(\text{bpy})_2 \text{ Cl}]^{3+}$ , where pOp is 4,4'-bipyridyl, bpy is 2,2'-bipyridyl and 4-tet is 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine.



As illustrated in Figure 1, the voltammetric response associated with the  $\text{Os}^{2+/3+}$  reaction is unusually ideal for both metal centers.



**Figure 1.** Voltammetric response for a 5  $\mu\text{m}$  platinum electrode modified with a monolayer of  $[\text{pOp Os}(\text{bpy})_2 \text{ 4-tet Os}(\text{bpy})_2 \text{ Cl}]^{3+}$ . The scan rate is 10 V/s. The supporting electrolyte is 1.0 M  $\text{LiClO}_4$  in acetonitrile. The monolayer surface coverage is  $9.8 \times 10^{-11} \text{ mol cm}^{-2}$ .

The formal potential of the inner redox center,  $[\text{pOp Os}(\text{bpy})_2 \text{ 4-tet}]^{2+}$ , is more positive than that of the outer moiety. Therefore, a fully oxidized monolayer (two  $\text{Os}^{3+}$  centers) may be reduced by two distinct mechanisms. First, both centers may undergo heterogeneous electron transfer. This mechanism would involve a through-bond distance of approximately 24 Å for the outer redox center. Second, the inner metal center could undergo short range heterogeneous electron transfer followed by electron cross-exchange between the outer and inner redox centers. A second heterogeneous electron transfer to the inner site would then complete the reduction process. Significantly, such a mechanism would allow the dynamics of the potential independent cross-reaction to be probed. We have addressed this issue using chronoamperometry conducted on a nanosecond timescale. Moreover, by comparing the electron transfer rates for electrochemically and photochemically driven process, we reveal the profound impact that differences between the energies of redox and bridge states can have on the dynamics of electron transfer.

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